STUDY OF CHROMIUM (VI) ADSORPTION USING *PTEROSPERMUM-ACERIFOLIUM* FRUIT CAPSULE ACTIVATED CARBON (FCAC) AND COMMERCIAL ACTIVATED CHARCOAL (CAC) AS A SELECTIVE ADSORBENTS

NAVIN CHANDRA KOTHIYAL, SUMIT SHARMA

Dr. B.R. Ambedkar National Institute of Technology, Jalandhar, India
 e-mail: kothiyalnc@nitj.ac.in

In the present study, fruit capsule activated carbon (FCAC) of *P-acerifolium* and commercial grade activated charcoal (CAC) were used for the study of adsorption of chromium (Vl) from aqueous solution. The maximum adsorption took place in the pH range of 3-6 with in contact time of 180 minutes. The adsorption kinetic of chromium (Vl) analyzed by pseudo first-order and pseudo second-order kinetics models. The kinetics of chromium (Vl) uptake was best described by pseudo-second order rate model (regression coefficients, $R^2 > 0.99$) with equilibrium rate constant values of 2.70 and 1.42 g/mg.min. for FCAC and CAC adsorbents. Intraparticle diffusion studies showed that the intraparticle transport is not only the rate-limiting step for the mechanism of chromium (Vl) adsorption. The experimental results presented indicated that the adsorption data fitted better with the Langmuir isotherm equation with regression coefficient $R^2 > 0.99$ for both the adsorbents. The maximum monolayer adsorption capacity of FCAC and CAC found to be 76.92 and 71.42 mg/g at initial pH 3.0. Thermodynamic parameters showed that adsorption process was spontaneous and endothermic. A comparative study of FCAC with commercial activated charcoal (CAC) showed that the adsorption capacity of indigenously prepared FCAC adsorbent was much better.
Key words: *P-acerfolium,* Chromium (VI), FT-IR, SEM-EDX, Adsorption Isotherm.

Studija adsorpcije kroma (VI) pomoću *Pterospermum-acerifolium* voćnih kapsula aktiviranog drvenog ugljena (FCAC) i komercijalnog aktiviranog drvenog ugljena (CAC) kao selektivnih adsorbensa. U ovom radu za studiju adsorpcije kroma (VI) iz otpadnih voda korištene su voćne kapsule aktiviranog ugljena (FCAC) *P-acerifolium* i komercijalni aktivirani drveni ugljen. Maksimalna adsorpcija odvijala se u pH području 3-6 pri vremenu kontakta od 180 minuta. Kinetika adsorpcije kroma (VI) analizirana je pseudo prvim i pseudo drugim kinetičkim modelom. Kinetika vezanja kroma (VI) najbolje se opisuje kinetičkim modelom pseudo drugog reda (koeficijent regresije, $R^2 > 0.99$) s konstantom ravnoteže od 2.70 i 1.42 g/mgmin za FCAC i CAC adsorbense. Studija međučestične difuzije prikazuje da međučestični transport nije jedini ograničavajući korak za adsorpcijski mehanizam kroma (VI). Prikazani eksperimentalni podaci ukazuju da se adsorpcijski podaci najbolje opisuju jednadžbom Langmuirove izoterme s koeficijentom regresije $R^2 > 0.99$ za oba adsorbensa. Maksimalni adsorpcijski kapacitet u jednom sloju na FCAC i CAC iznosi 76.92 i 71.42 mg/g za početni pH 3.0. Termodinamički parametri pokazuju da je adsorpcijski proces spontan i endoterman. Usporedna studija FCAC s komercijalnim aktiviranim drvenim ugljenom (CAC) pokazuje da je adsorpcijski kapacitet izvorno pripremljenog FCAC adsorbensa mnogo bolji.
Ključne riječi: *P-acerfolium,* krom (VI), FT-IR, SEM-EDX, adsorpcijska izoterma.

INTRODUCTION

The excessive heavy metal ions in wastewater are producing a major problem for the living bodies. These heavy metal ions are non-biodegradable and accumulate in living organisms causing various types of disorders such as lung cancer, as well as kidney, liver, and gastric damage [1]. Chromium (VI) is highly toxic element in the environment. Its toxicity include dermatitis, damage to liver, kidney circulation, nerve tissue damage, and death in large doses while ingestion may cause epigastric pain, nausea, severe diarrhoea, haemorrhage and vomiting [2-3]. The contamination of wastewater in many industries, such as metal plating facilities, mining operations, tanneries, etc. are often associated with cadmium, chromium, lead and mercury metals [4].

However, chromium (Vl) is one of the key contaminants in the wastewaters of many industries such as; dyes and pigments, metal cleaning, plating and electroplating, leather and mining [5]. The concentration of chromium (Vl) in industrial wastewater may be from 10 to 100 mg/dm^3 which is much higher than standard limit of 0.1 mg/ dm^3 [6-8]. Hence, there is a need to treat the wastewaters containing toxic metals (chromium (Vl)) before their discharge into the waterbodies and reduce their concentrations to the acceptable level. In recent years, many physico-chemical methods employed for the removal of chromium (Vl) or other metal ions from various types of solutions. A few of among them were Reduction followed by Chemical precipitation [9], Activated sludge [10], Cementation [11], Evaporators [12], Ion exchange resins [13], and Electrocoagulation methods [14].

The high operation cost, handling and disposal problems and high sludge production, however limit their uses in wastewater treatment. Therefore, it is necessary to develop suitable technologies that should be inexpensive and highly efficient in removal of heavy metals from wastewater. In view of the above, adsorption method is considered to be one of the preferable method for the removal of chromium (Vl) or other metal ions from aqueous solution due to its significant advantages such as; low operational cost, widely applicable and creates relatively low sludge [1, 4, 8, 15-20]. Nowadays, activated carbon is an effective and inexpensive adsorbent [15,21-23] and has been widely used in the treatment of wastewater due to its exceptionally high surface areas which range from 500-1500 m^{2}g^{-1}, well developed internal microporosity structure and presence of a wide spectrum of surface functional groups [3,21]. Activated carbons are extremely versatile adsorbents of industrial significance and used in a wide range of applications that are concerned principally with removal of undesired species by adsorption from liquids or gases [24].

The activated carbon can removes heavy metals by various mechanisms; however, complexation or electrostatic attraction of metal ions to various surface oxygen-containing functional groups is the most appropriate [21-22]. Nowadays, there is a tremendous demand to produce low cost alternatives for activated carbon that should be effective and abundant in nature [19-20]. In addition, considerable work also carried out for the effective removal of chromium by using activated carbon prepared from low cost materials that are widely available and environment friendly [5, 25-28].

Generally, the activated carbon is prepared by chemical activation due to the development of better porous structure as well as the high conversion of the precursor to carbon can be obtained as a result of the inhibition of tar production by chemical agents, hence enhancing the carbon yield

[25]. This study is likely to evaluate the effectiveness and feasibility of low cost activated carbon as a potential adsorbent for the removal of chromium (Vl) from aqueous solution. *Pterospermum-acerifolium* is an Indian angiosperm tree indigenous to southeast Asia, from India to Burma having fragrant nocturnal white flowers and yielding a reddish wood used for planking.

The best growing conditions are a seasonally moist then dry climate with access to full sunlight. The fruit capsules of *p-acerifolium* are abundantly available and act as biowaste in the nature, which are cheap as well as environmentally friendly. Thus, the process of activated carbon preparation from these unused fruit capsules can be technically feasible alternative for the

removal of chromium (Vl) metal ions from aqueous solutions.

The purpose of this investigation was to prepare activated carbon from low cost biowaste material (fruit capsule of *P-acerifolium*) available in the local area for the removal of chromium (Vl) ions from aqueous solution and to find optimum adsorption isotherm as well as the adsorption kinetic model. The comparative study with commercial grade activated charcoal (CAC) for the adsorption of chromium (Vl) under the same experimental protocols was also carried out.

Adsorbent dosages, pH, contact time and initial chromium (Vl) concentration were the parameters investigated in the present study.

MATERIALS AND METHODS

Materials

All solutions were prepared from analytical reagent grade chemicals procured from Merck Specialty Chemicals, Pvt. Ltd. Mumbai, India by using Milli-Q filtered deionized water. Synthetic stock solution ($1000mg/dm^3$) of chromium (Vl) was prepared by dissolving required quantity of $K_2Cr_2O_7$ (Atomic wt., 294.14) in deionized

water. For adsorption experiments, working solutions of chromium (Vl) having concentration in between 2-10 mg/dm^3 was prepared by serial dilution using micropipette.

The pH of the solutions adjusted either with diluted HCl or with NaOH solutions.

Glasswares

All glasswares of Borosil make glass (A grade) were used in the study. Glasswares

dipped in dilute Nitric acid and washed with double distilled water every time before use.

Preparation of adsorbent

The raw material choosen in the present study was available in plenty in southeast Asia and Indian subcontinent regions. The classification of fruit capsule source (*P-acerifolium*) described in Table 1. The fruit capsules of *P-acerifolium* collected from the Jalandhar campus. The fruit

capsules were washed with distilled water to remove any colour and impurities adhere to the surface of the fruit capsules. The outer granular part of the fruit capsule was taken out by mechanical scratcing with spatula/knife. The granular part of the fruit

capsule then air-dried at 353±1K for 24 hours and stored in a vacuum desiccators.

The product obtained was then grounded and fine powder of the material was obtained. The material was then sieved to 500 μm particle size by standard sieve. The resulting material preserved in the airtight dry bottle. Commercial grade activated charcoal (CAC) choosen for comparison in the present study procured from Quligens fine chemicals pvt. Ltd, Mumbai, India and used without any chemical pre-treatment.

The activated carbon was derived from fruit capsule of *p-acerifolium* by using the chemical method as described by earlier workers [5, 29-33].The prepared material was mixed with 1 N H_2SO_4 (98%) in appropriate ratio (1:1,wt) and then allowed to soaked for 24 hours at room tempreture.

The material was heated at 473±1K with intermitted stirring for 24 hours in the oven and then allowed to cool back at room tempreture and washed with distilled water and soaked in 1%$NaHCO_3$ solution to remove any remaining acid on the surface.

The remaining product was then again washed with distilled water and dried again at 378±1K for 24 hours.The fruit capsule of *p-acerifolium* and prepared activated carbon from them were shown in Fig.1(a) and (b).

Table 1. Classification of *P-acerifolium*
Tablica 1. Klasifikacija *P-acerifolium*

Kingdom	Plantae
Order	Malvales
Family	Malvaceae
Genus	Pterospermum
Species	P.acerifolium
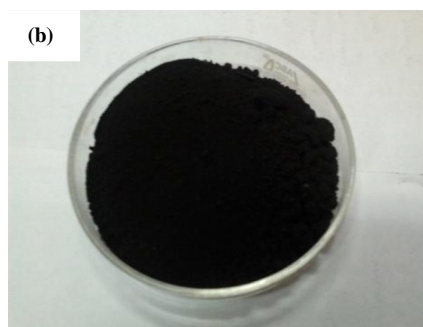
Figure 1. (a) Fruit capsule as a source of activated carbon [34]; (b) FCAC adsorbent used
Slika 1. (a) Voćne kapsule kao izvor aktiviranog ugljika; (b) korišteni FCAC adsorbens

EXPERIMENTAL PROCEDURE

The adsorption experiment were carried out in which aliquots of 50 cm^3 of chromium (Vl) solution of known concentrration were pour into separate 250 cm^3 conical flasks containing accuretely weighed amounts of the adsorbents. The adsorbents weight ranged from 0.2 to 1.0 g in 50 cm^3 of solution while the initial chromium (Vl) concentration maintained at 10 mg/dm^3.

The conical flasks were uniformly shaken at optimum speed using electric wrist action shaker for fixed time intervals from 30 to 180 minutes at a tempreture of 303±1K. The solution was then filtered through A-grade whatman no.1 filter paper with the help of vaccum pump and the filtrate preserved for residual chromium (Vl) ion concentration determination by Atomic Absorption Spectrophotometer (Model AAS 4129, ECIL, India) at a wavelength of 357.8 nm.

The percent removal of chromium (Vl) in solution was calculated by following equation:

$$\text{Removal (\%)} = \frac{(C_i - C_t)}{C_i} \times 100 \quad (1)$$

C_i and C_t were the concentrations of chromium (Vl) initially and at a given time t in the solution.

RESULTS AND DISCUSSION

SEM-EDX for morphology and elemental analysis of FCAC

SEM-EDX pictures of fruit capsule activated carbon (FCAC) prepared in this study were shown Fig.2 and 3. It usually revealed the surface texture and their different porosity levels in the adsorbent. SEM picture of FCAC adsorbent showed that the surface of FCAC had irregular uneven small size particles and had little porous nature (Fig.2). EDX spectrum analysis of the FCAC indicated some prominent peaks due to silicon, aluminum, nitrogen, potassium, oxygen and carbon elements [4, 35] as shown in Fig.3 and Table 2. These elemental distribution revealed that carbonyl, amines, and −OH groups may be predominantly present on the surface of FCAC which were also detected in FT-IR spectrum (Fig.4).

Identification of chromium (Vl) binding functional groups

The capacity of activated carbon to adsorb chromium (Vl) ions depend on the quantity of surface functional groups [21]. The carbon atoms that localized at the edges and the periphery of the aromatic sheets or those located at defect position and dislocations or discontinuities were associated with unpaired electron or have residual valancies; these were rich in potential energy. These carbon atoms were more reactive and have a tendency to form surface oxygen complexes during activation. These surface chemical groups may promote chromium (Vl) adsorption [24].

Table 2. Chemical composition of FCAC adsorbent
Tablica 2. Kemijski sastav FCAC adsorbensa

Elements	Percent composition
C	24.3
N	1.17
O	65.8
Al	2.09
Si	5.19
Other	1.33

FT-IR study of FCAC was carried out by using a FT-IR technique to detect the active functional groups responsible for the adsorption of chromium (Vl) from aqueous solution. The FT-IR spectrum along with assignment of the peaks in the spectrum of FCAC showed in Fig.4 and Table 3 [32, 35-36].

The ionization of the surface functional groups leaves some vacant sites that might have been replaced by chromium (Vl) metal ions [37].

Table 3. Some prominent Peaks from FCAC spectrum and their possible assignment
Tablica 3. Neki istaknuti pikovi FCAC spektra I njihova moguća pripadnost

Band positions(cm^{-1})	Assignments
1173	>S=O, symmetrical stretching
797	>S-O, stretching
1709	>C=O, stretching band
464	Metal halogen bond
1610	>N-H, primary amine
2923	>C-H stretching vibration (alkenes)
3422	H-bonded –OH groups

Effect of adsorbent dosage

The effect of adsorbent dosages on the percent removal of chromium (Vl) and variation of amount of chromium (Vl) adsorbed per unit weight of the adsorbents have been illustrated in Fig. 5 (a) and (b). Amount of FCAC and CAC were varied from 0.2 to 1.0 g and equilibrated for 60 minutes, pH of solution was 6 and temperature was maintained at 303±1K. The results indicated that the percent removal of chromium (Vl) increased from 85.1 to 99.5% for FCAC and 74.4 to 91.9% in case of CAC while adsorption capacity tends to decreased from 42.55 to 9.95 mg/g for FCAC and 37.2 to 9.19 mg/g of CAC with increases in the amount of both FCAC and CAC adsorbents.

The increases in the percent removal of chromium (Vl) from the aqueous solution with increase in the adsorbent dosages were attributed due to the greater availability of exchangeable sites on (FCAC and CAC) adsorbents for metal ions as noticed by [38-

39]. As the surface adsorption sites became exhausted, uptake was controlled by the rate at which the chromium (Vl) was transported from the exterior to the interior sites of the FCAC and CAC adsorbents. When the adsorbent doses reached higher, the adsorption process undergoes saturation that can be attributed due to the resistance to mass transfer of chromium (Vl) from bulk liquid to the surface of the solid [33]. The decrease in the amount of chromium (Vl) adsorption per unit weight of both the adsorbents (FCAC and CAC) were attributed due to electrostatic interactions, interference between binding sites, and reduced mixing at higher adsorbent densities [40]. Tazrouti and Amrani [7], Isa et al [33] and Zvinowanda et al [4] also obtained similar kind of results.

Effect of contact time

The equilibrium time for the adsorption of chromium (Vl) onto FCAC and CAC adsorbents has been studied. The variation in percent removal of chromium (Vl) with the time has been shown in Fig.6. Fig.6 indicated that 56.8% removal of chromium (Vl) took place in first 30 minutes which increased up to 96.1% for FCAC in 180 minutes. In case of CAC, the initial removal rate was 48.9% and after 180 minutes percent removal of chromium (Vl) reached to 92.8%. The rate of adsorption was rapid in the beginning and becomes slightly saturated with increase in contact time of chromium (Vl) with adsorbents. Nomanbhay and Palanisamy [41], Hasar and Cuci [29] and Vinodhini and Das [18] also found similar kind of results. It might be due to larger surface area having large number of vacant sites available for adsorption at initial time. After a few minutes, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between chromium (Vl) adsorbed on the surface of the adsorbents and in solution in the form of $HCrO_4^{-}$, $Cr_2O_7^{2-}$, CrO_4^{2-} ions [7].
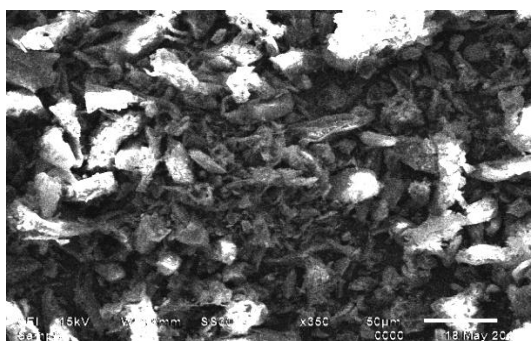
Figure 2. SEM photograph of FCAC
Slika 2. SEM snimka FCAC
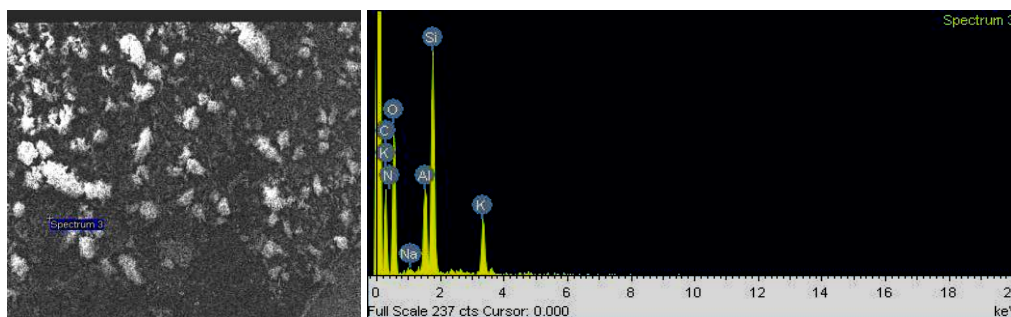
Figure 3. SEM microstructure and EDX Spectrum of FCAC
Slika 3. SEM mikrostruktura i EDX spektar za FCAC

Effect of pH of solution

The pH of the aqueous solution is one of the key factors that control the adsorption process of chromium (Vl) because it controls the electrostatic interactions between the adsorbents and the adsorbate. The adsorption studies at different pH values conducted at the pH range of 1 to 12. The maximum adsorption capacities of chromium (Vl) for both FCAC and CAC were observed between pH 3-6 and sharply decreased with the increase of pH values beyond 6 as shown in Fig.7. As the pH increased, initially a little increase in the adsorption capacities were observed from pH 1 to 3 and becomes maximum between pH 3-6 in both the cases (FCAC and CAC).

At lower pH, the surfaces of the adsorbents positively charged due to protonation that leads to electrostatic attraction with anionic species of chromium (Vl) in the solution $HCrO_4^{4-}$, CrO_4^{2-}, $Cr_2O_7^{2-}$ and other chromium oxyanion states [16, 42-43]. However, Zvinowanda et al explained that at low pH, there were large numbers of H^+ ions, which in turn neutralize the negatively charged adsorbents surface thereby reducing hindrance to the diffusion of dichromate ions [4]. When the pH values further increased above pH 6, sharp decreases in the adsorption capacities observed.

The decreases in adsorption capacities beyond pH 6 might be due to occupation of the adsorption sites by anionic species like $HCrO_4^{4-}$, $Cr_2O_7^{2-}$, and CrO_4^{2-}, which retards the approach of such ions further towards the adsorbents surface due to electrostatic repulsion between negative surface charge and chromium (Vl) anions and between chromium-chromium (Vl) anions in the solution [18, 44-45]. Babu and Gupta demonstrated that maximum removal of chromium (Vl) took place in the acidic pH of solution (1-3) which decreased sharply with the increase in the initial pH = 5 to pH = 11 [17].

However, Sarin and Pant explained that percent removal of Cr (VI) decreased from 99 to 93 % with increasing pH from 1.5 to 5, whereas as the pH increased from 5 to 9 the percent removal decreased significantly from 93 to 63 % [1]. The decreases in adsorption capacities at higher pH values were attribute due to the competitiveness of the oxyanion of chromium (Vl) and OH^- ions in the bulk as observed by Attia et al [32].

Effect of initial concentration of chromium (Vl)

The effect of adsorption of chromium (Vl) at different initial concentrations (2-10 mg/dm^3) of FCAC and CAC were investigated and shown in Fig.8. The maximum adsorption by both FCAC and CAC (1g/50 cm^3) took place at lower concentration of chromium (Vl) at an optimized pH=3 and contact time of 180 minutes. This was because at lower concentration there were sufficient active sites on the surface that the adsorbate can easily occupy. However, at higher concentrations, active adsorption sites were not sufficiently available for the adsorbate to occupy. Hence, chromium (Vl) was not completely adsorbed in solution due to the saturation of binding sites [32]. As the concentration of chromium (Vl) increased from 2 to 10 mg/dm^3 the percent adsorption was decreased simultaneously from 49 to 12.7% for FCAC and 45.5% to 12% in case of CAC.

Adsorption isotherms

Adsorption studies carried out with a fixed initial adsorbent dosage 1.0 g, pH =3 and by varying chromium (Vl) concentration. During the adsorption process, a rapid equilibrium established between adsorbed chromium (Vl) ions on the adsorbent (q_e) and unadsorbed chromium (Vl) ions in solution (C_e) as represented by the Langmuir or Freundlich adsorption isotherms. In the present study, equilibrium of adsorption of chromium (Vl) was modelled using Langmuir and Freundlich isotherm to describe the adsorption equilibrium over entire concentration range studied. The adsorption equilibrium studies carried out at room temperature 303±1K. The general non-linear form of Freundlich isotherm model was [46]

$$q_e = k_f C_e^{1/n} \quad (2)$$

Where k_f (mg/g) stands for adsorption capacity, C_e (mg/dm^3) for equilibrium concentration of chromium (Vl) and n (g/dm^3) for adsorption intensity. A linear form of the Freundlich isotherm obtained by taking the logarithmic of Eq. (2):

$$Log q_e = Log K_f + \frac{1}{n} Log C_e \quad (3)$$

In Langmuir Isotherm the solute uptake controlled by monolayer adsorption on a homogeneous surface having a finite number of identical sites, each site can hold only one adsorbate molecule (the adsorbed layer is one molecule in thickness) and there is no interaction between adsorbed molecules [47]. The linear form of Langmuir isotherm represented in the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{C_e}{q_{max}} \quad (4)$$

Where q_e was amount of chromium (Vl) adsorbed per unit weight of adsorbent (mg/g), q_{max} was the maximum monolayer adsorption capacity (mg/g) and b was the Langmuir constant (dm^3/mg). Table 4 presented the isotherm parameters for linearized Langmuir and Freundlich isotherm models as shown in Fig.9 and 10. The adsorption isotherm studies clearly indicated that the adsorptive behavior of chromium (VI) satisfies both Langmuir and Freundlich assumptions. The linear regression coefficients of both models showed a strong affinity for the adsorption

of chromium (Vl) on both the adsorbents (Table 4). However, the linear regression coefficients $(R^2 > 0.99)$ of the Langmuir isotherms proved that Langmuir isotherm model exhibit better fit to the experimental data of FCAC as well as CAC rather than Freundlich isotherm models. It can be said that the atoms at the surface of solids have some imbalanced forces as compared to those within the solids and, consequently, foreign molecules (chromium (Vl)) in a bid to satisfy this imbalance get attracted to the surface and form a monolayer on the surface of the solids (FCAC and CAC) [24].

As a result, monolayer adsorption took place on the homogeneous surface of the adsorbents with all sites have equal adsorption energies and there were no interaction among adsorbed molecules. The constant (q_m) maximum monolayer adsorption capacities, were found to be 76.92 and 71.42mg/g for FCAC and CAC at the initial pH=3 while the values of constant

b, which denotes adsorption energy, were equal to 3.25 and 1.40 dm^3/mg, respectively. The n (adsorption intensity) value of Freundlich varies inversely with the slope that defined by $1/n$. The slopes $(1/n)$ of Freundlich isotherm found to be 0.122 and 0.133 for FCAC and CAC. The values of $1/n$ < 1 indicated favorable adsorption irrespective of treatment [5]. The q_{max} value of the Langmuir model and k_f value of the Freundlich model both indicated that the adsorption capacity of FCAC to adsorb chromium (Vl) was more as compared to CAC.

In order to determine the nature of adsorption process whether favorable or unfavorable, the dimensionless constant separation term (R_L) investigated and expressed as

$$R_L = \frac{1}{(1+bC_0)} \quad (5)$$
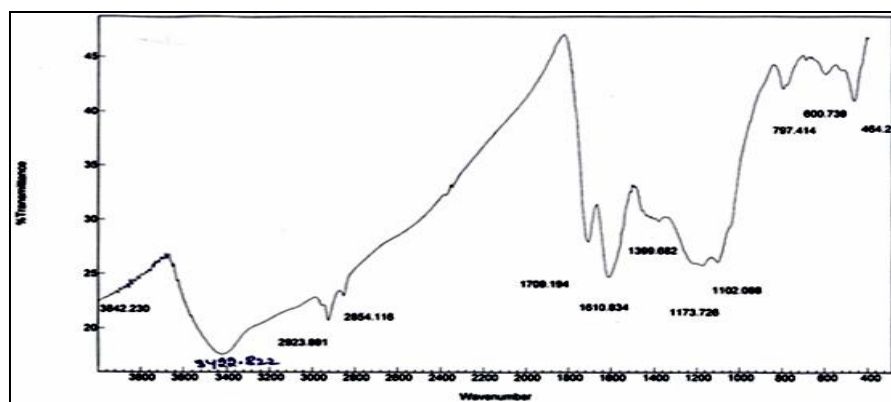
Figure 4. FT-IR Spectrum of FCAC
Slika 4. FT-IR spektar za FCAC

R_L values indicated the nature of adsorption process as given below [7]:

R_L values	Adsorption
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

In the present investigation, the dimensionless parameter (R_L) values were found to be 0.029 and 0.066 ($0 < R_L < 1$) for the FCAC and CAC which showed that adsorption of chromium (Vl) onto both the adsorbents (FCAC and CAC) were thermodynamically favourable process [22].

Comparison of the adsorption capacities with other activated carbons

The maximum adsorption capacity for chromium (Vl) by activated carbon prepared from different sources and FCAC used in the present study were given in Table 5. Although direct comparison of FCAC used with other reported activated carbon was difficult due to the varying experimental conditions employed in those studies, the data showed that FCAC has generally a reasonable higher adsorption capacity than various other activated carbons. It was also noteworthy that the adsorption capacity of FCAC adsorbent found to be comparable with commercial activated carbon FS-100 (69.30 mg/g) and SHT (69.10 mg/g) at acidic pH=3 as noticed by Hu et al [3, 48]. However, the adsorption capacity of FCAC was lower than activated carbon prepared from Hazelnut Shell (170.0 mg/g) [28].

Adsorption kinetics

In order to investigate the mechanism of chromium (Vl) adsorption onto the FCAC and CAC adsorbents, different kinetic models were tested.

Pseudo first-order equation

According to pseudo-first order, rate equation the rate of change of chromium (Vl) uptake with time should be directly proportional to the difference in the saturation concentration and the amount of solid uptake with time. The linear form of pseudo first-order equation expressed as [51]:

$$Log(q_e - q_t) = Logq_e - \frac{k_1}{2.303}t \quad (6)$$

The values of $Log (q_e - q_t)$ were linearly correlated with t (adsorbent dosage 1.0 g, pH 3.0, and T = 303±1 K) and the plot of $Log (q_e - q_t)$ versus t must give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively. Fig.11 showed the pseudo-first order kinetic plot for the adsorption of chromium (Vl) onto the FCAC and CAC adsorbents. The calculated k_1, q_e and their corresponding linear regression coefficient values represented in Table 6.

Pseudo second-order equation

The pseudo-second-order reaction greatly influenced by the amount of chromium (Vl) on the adsorbent surface and the amount of chromium (Vl) adsorbed at equilibrium. The linear form of pseudo second-order adsorption rate equation expressed as [52]

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (7)$$

Where h (mg/g. min) was the initial adsorption rate as $t \rightarrow 0$ i.e.

$$h = k_2 q_e{}^2$$

k_2 (g/mg. min) was the equilibrium rate constant of pseudo second order equation. Where q_e (mg/g) and q_t (mg/g) were the adsorption capacities at equilibrium and at given time t. Fig.12 represented the linearized plot of pseudo second-order kinetic model. The plot for pseudo second order model yields very good straight lines and the correlation coefficients, ($R^2 > 0.99$) were also lies in good agreement with pseudo second-order kinetic models for both FCAC as well as for CAC adsorbents as shown in the Table 6. Hence, pseudo second-order kinetics was supposed to be the best-fit model to explain the present experimental data for FCAC and CAC adsorbents and suggested that chemisorption was the rate-controlling mechanism for the adsorption process [33].

Intraparticle diffusion equation

Intraparticle-diffusion model also tested for adsorption studies by FCAC and CAC adsorbents. The intraparticle diffusion equation expressed as:

$$q_t = k_{id}\, t^{1/2} + C \quad (8)$$

Where, C was the intercept and K_{id} (g/mg.min$^{1/2}$) was the constant coefficient, the initial rate of intraparticle diffusion (mg/dm^3.min$^{1/2}$). The plot of q_t vs. $t^{1/2}$ gave straight line consisting of two segments as shown in Fig.13.The constants C and K_{id} values of FCAC and CAC calculated from the given plot were represent in Table 6. The first linear segment, with a steeper slope, attributed to the boundary layer (film) diffusion of the chromium (Vl). The second segment of the line indicated a gradual adsorption stage, characterized by the intra-particle diffusion of chromium (Vl) in the adsorbent surface.

The slope of each linear portion described the rate of the corresponding adsorption; a lower slope described a slower adsorption process [53]. It proved that the boundary layer diffusion proceeds faster than the intra-particle diffusion in the present study. Furthermore, the second linear segment of the line, describing the intra-particle diffusion, does not pass through the origin indicated that the intra-particle diffusion, was not only the rate-limiting step in the adsorption process.
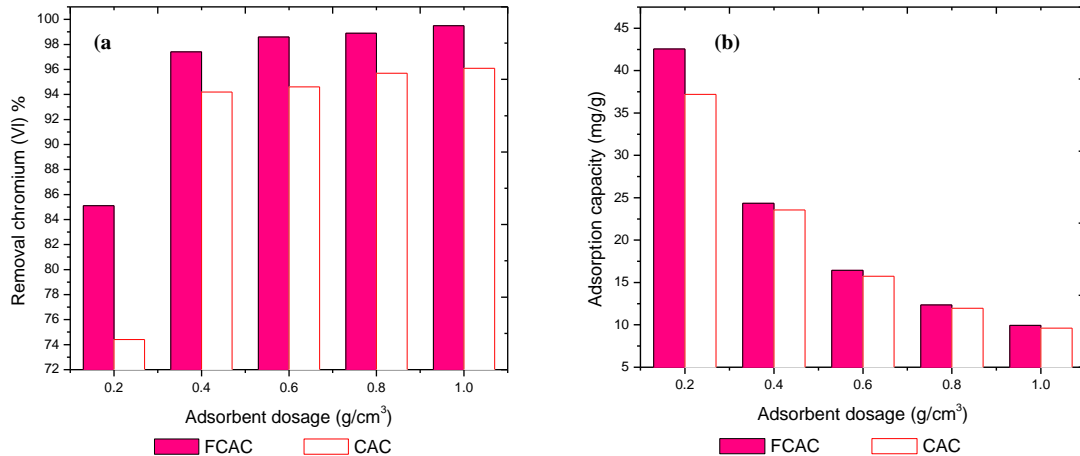
Figure 5. Effect of adsorbent dosage (g/50cm³) on Cr (VI) adsorption (a) % removal; (b) Change of adsorption capacity (Initial concentration of Cr (VI), 10 mg/dm³; pH, 6.0; contact time, 1h; T = 303±1K)

Slika 5. Utjecaj količine adsorbensa (g/50cm³) na adsorpciju Cr (VI) (a) % uklanjanja; (b) promjena adsorpcijskog kapaciteta (početna koncentracija (Cr (VI), 10 mg/dm³; pH, 6.0; vrijeme kontakta, 1h; T = 303±1K)
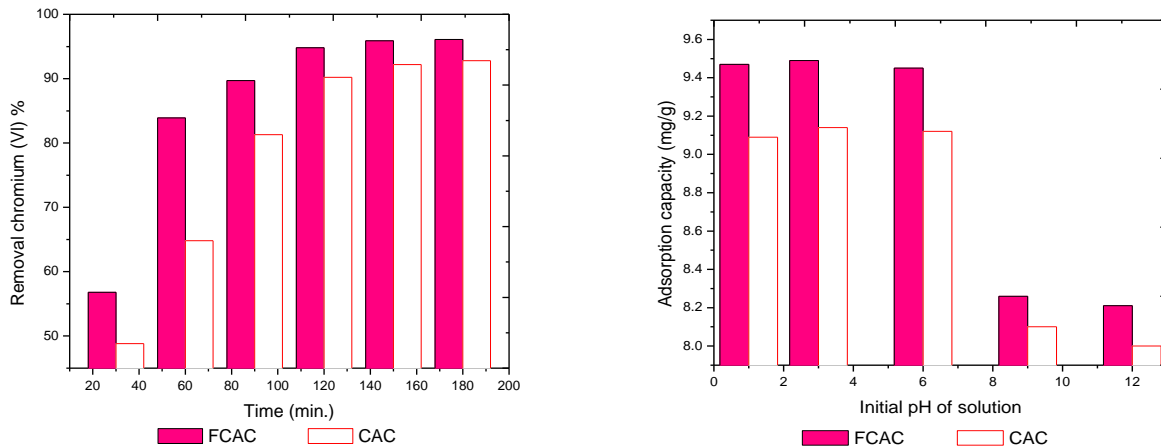
Figure 6. Effect of Contact Time on Cr (Vl) adsorption (Concentration of Cr (VI), 10 mg/dm³; Adsorbent dosage; 1g /50 cm³; T = 303±1K)

Slika 6. Utjecaj vremena kontakta na adsorpciju Cr (VI) (koncentracija Cr (VI), 10 mg/dm³; količina adsorbensa; 1g /50 cm³; T = 303±1K)

Figure 7. Effect of pH on Cr (VI) adsorption (Concentration of Cr (VI), 10 mg/dm³; pH, 6.0; Adsorbent dosage, 1g/50cm³; T = 303±1 K)

Slika 7. Utjecaj pH na adsorpciju Cr (VI) (koncentracija Cr (VI), 10 mg/dm³; pH, 6.0; količina adsorbensa, 1g/50cm³; T = 303±1 K)

Thermodynamics studies on adsorption of chromium (Vl)

Thermodynamic parameters evaluated to predict the nature of adsorption of chromium (Vl) on the adsorbent. Gibbs free energy (ΔG), enthalpy change (ΔH) and entropy change (ΔS) were some of the important thermodynamic parameters that were calculated. The values of thermodynamic constants: entropy change (ΔS) and enthalpy change (ΔH) computed from the slope and intercept of the plot of *Log k_c vs 1/T* (Fig.14). The values of ΔS and ΔH were calculated using following relation:

$$Log k_C = \frac{\Delta S}{R} - \frac{\Delta H}{2.303}RT \quad (9)$$

The Gibbs free energy (ΔG) of an adsorption process obtained from equation:

$$\Delta G = -RT \ln (k_C) \quad (10)$$

Where k_c was the equilibrium constant, ΔG was the Gibbs free energy change (kJ/mol), T was the absolute temperature (K), and R was the universal gas constant (8.314 J / mol. K). The values of ΔG of the process found to be negative and decreased with the rise in temperature from 303 to 343K that means the adsorption process was spontaneous and the degree of spontaneity of the reaction was increases with increase of temperature (Table 8) [7-8]. Thermodynamic parameters for the adsorption of chromium (Vl) by some other adsorbents and adsorbents used in this study were compared and tabulated in Table 7. In most cases, adsorptions of chromium (Vl) found to have negative values of ΔG as outlined in Table 7. The overall adsorption process seems to be endothermic (ΔH=3.66 and 3.47 KJ/mol for FCAC and CAC, respectively) as illustrated in Table 8.
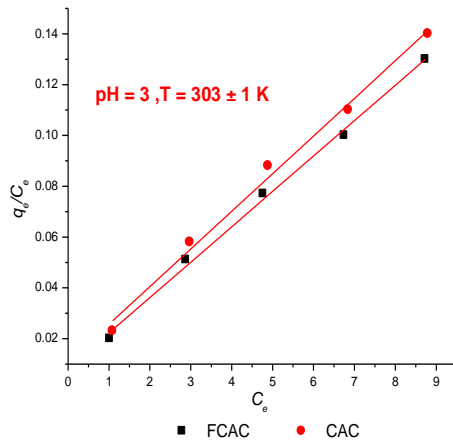
The positive value of ΔS suggested increase in the randomness at the solid/solution interface due to the redistribution of energy between the adsorbent and chromium (Vl). The positive value of ΔS for the adsorption of chromium (Vl) by the adsorbents used in this study were also agree with those of others adsorbents given in Table 7.
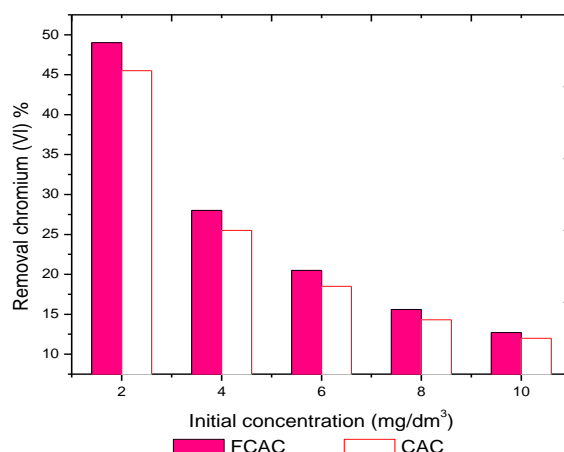
Figure 8. Effect of Initial concentration on Cr (VI) adsorption (Adsorbent dosage, 1g/50 cm^3; pH 3.0; T = 303±1K)
**Slika 8**. Utjecaj početne koncentracije na adsorpciju Cr (VI) (količina adsorbensa, 1g/50 cm^3; pH 3.0; T = 303±1K)

However, a negative value for *ΔS* also reported for the adsorption of chromium (Vl) by Baggase fly ash. Before adsorption occurs, the chromium (Vl) near the surface of the adsorbents will be more ordered than in the subsequent adsorbed state and the ratio of free chromium (Vl) to ions interacting with the adsorbent will be higher than in the adsorbed state. As a result, the distribution of rotational and translational energy among a small number of molecules will increase with increasing adsorption by producing a positive value of *ΔS* and randomness will increase at the solid-solution interface during the process of adsorption [54].

Figure 9. Langmuir isotherm for Cr (VI) adsorption
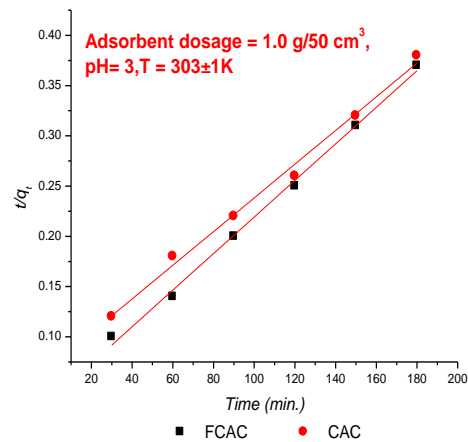**Slika 9**. Langmuirova izoterma za adsorpciju Cr (VI)
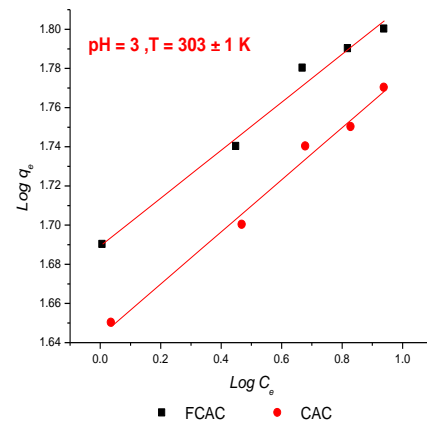
Figure 10. Freundlich isotherm for Cr (Vl) adsorption
Slika 10. Freundlichova izoterma za adsorpciju Cr (VI)
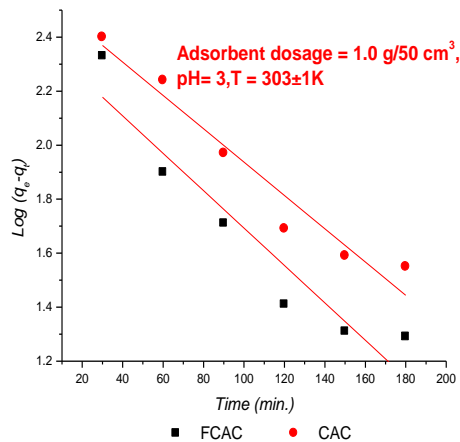
Figure 11. Pseudo-first order kinetic plot for adsorption of Cr (VI)
Slika 11. Dijagram kinetike pseudo prvog reda za adsorpciju Cr (VI)

Figure 12. Pseudo-second order kinetic plot for adsorption of Cr (Vl)
Slika 12. Dijagram kinetike pseudo drugog reda za adsorpciju Cr (VI)

Table 4. Equilibrium isotherm parameters for Cr (VI) adsorption[a]
Tablica 4. Ravnotežni parametri adsorpcijske izoterme za Cr (VI)

Adsorbent	Langmuir Isotherm				Freundlich Isotherm		
	(q_{max})	(b)	(R_L)	(R^2)	$(1/n)$	(K_f)	(R^2)
FCAC	76.92	3.25	0.029	0.996	0.122	5.41	0.986
CAC	71.42	1.40	0.066	0.993	0.133	5.17	0.989

[a] T = 303 ±1K, pH=3

Table 5. q (mg/g) for activated carbons prepared from various sources
Tablica 5. q (mg/g) za aktivirani ugljik dobiven iz različitih izvora

Raw material	q (mg/g)	pH	Ref.
Hazelnut shell	170.0	1.0	[29]
Hazelnut shell	17.7	2.0	[49]
T.A nuts [a]	28.4	1.0	[27]
RWS [b]	44.1	2.0	[50]
OS-Sulfuric acid AC[c]	71.4	1.5	[33]
FCAC	76.9	3.0	[T.W][d]

[a] Terminalia arjuna nuts; [b] Rubber wood sawdust; [c] Olive stone-sulphuric acid activated carbon; [d] This work

Table 6. Kinetic parameters for Cr (VI) adsorption [a]
Tablica 6. Kinetički parametri za adsorpciju Cr (VI)

Adsorbent	Pseudo first order			Pseudo second order			Intraparticle diffusion		
	(q_e)	(k_1)	(R_1^2)	(k_2)	(h)	(R_2^2)	(k_{id})	(C)	(R_3^2)
FCAC	10.85	0.013	0.908	2.70	27.02	0.996	22.92	205.3	0.805
CAC	12.85	0.011	0.947	1.42	14.28	0.993	29.08	105.5	0.929

[a] Conditions: T = 303 ±1K; pH=3

Table 7. Thermodynamic parameters for the adsorption of Cr (Vl) by different adsorbents
Tablica 7. Termodinamički parametri za adsorpciju Cr (VI) na različitim adsorbensima

| S.No.	Adsorbent	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol K)	Ref.
1.	Kraft lignin	Negative	-20.68	0.086	[7]
2.	Baggase fly ash	Negative	50.43	-112.76	[2]
3.	BRS	Negative	25.12	0.091	[55]
4.	Groundnut hulls	Positive	14.7	0.03	[56]
5.	Sulfonated lignite	Negative	14.16	63.62	[8]
6.	Modified oak sawdust	Negative	0.908	0.008	[54]
7.	Recinius Communis	Negative	4.89	0.023	[57]
8.	Carica Papaya Linn	Negative	5.20	0.029	[57]
9.	Morinda Pubescence	Negative	5.40	0.045	[57]
10.	FCAC	Negative	3.66	0.044	[T.W][a]
11.	CAC	Negative	3.47	0.042	[T.W] [a]

[a] This work

Table 8. Thermodynamic parameters for Cr (VI) adsorption [a]
Tablica 8. Termodinamički parametri za adsorpciju Cr (VI)

Adsorbent	(ΔS) (KJ/K.mol)	(ΔH) (KJ/mol)	Gibbs free energy change (ΔG)(KJ/mol)				
			303	313	323	333	343
FCAC	0.044	3.66	-1.03	-1.95	-2.85	-4.28	-5.27
CAC	0.042	3.47	-0.78	-1.48	-2.39	-3.65	-4.62

[a] Conditions: T = 303-343K, pH = 3.0, Adsorbent dosage = 1.0g/50 cm³
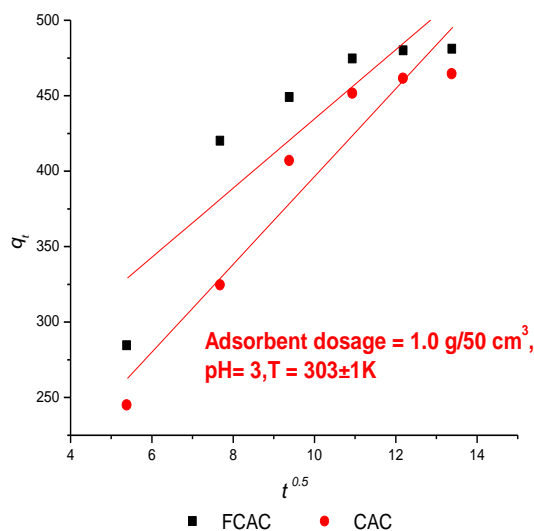
Figure 13. Intraparticle diffusion plot for adsorption of Cr (VI)
Slika 13. Dijagram međučestične difuzije za adsorpciju Cr (VI)
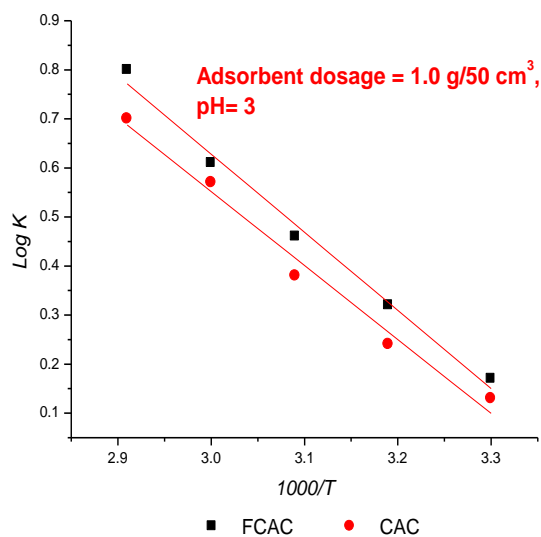
Figure 14. Effect of temperature on the adsorption of Cr (VI)
Slika 14. Utjecaj temperature na adsorpciju Cr (VI)

CONCLUSION

The FCAC adsorbent prepared from biological waste and commercial grade activated charcoal, CAC showed superior adsorption properties towards chromium (Vl) ions. However, adsorption capacity of FCAC found to be slightly higher than that of CAC under the similar experimental conditions. Adsorption of chromium (Vl) was highly pH dependent and the results showed that the optimum pH for the chromium (Vl) removal was between 3 and 6 at 303±1K for both the adsorbents. The adsorption isotherm for chromium (Vl) adsorption on FCAC and CAC at 303 ±1K was best represented by the Langmuir model ($R^2>0.99$) over entire concentration range studied and suggest that the surface is relatively homogenous in terms of functional groups.

The kinetics of chromium (Vl) adsorption on FCAC and CAC adsorbents follows pseudo-second order model with chemisorptions as the rate-controlling step. Thermodynamic data confirmed that chromium (Vl) adsorption reaction is endothermic and spontaneous.

Acknowledgement

REFERENCES

[1] V. Sarin and K.K. Pant, Bioresource Technology 97 (2006), 15-20.

[2] V. Gupta, D. Mohan, S. Sharma, K. Park, The Environmentalist 19 (1999), 129-136.

[3] M. Owlad, M.K. Aroua, W.A.W. Daud, S. Baroutian, Water Air Soil Pollut. 200 (1) (2008), 59-77. doi: 10.1007/s11270-008-9893-7.

[4] C. M. Zvinowanda, J. O. Okonkwo , P. N. Shabalala, N. M. Agyei, Int. J. Environ. Sci. Tech. 6 (3) (2009), 425-434.

[5] A. Esmaeili, S. Ghasemi, A. Rustaiyan, Journal of Marine Science and Technology 18 (4) (2010), 587-592.

[6] Y. Nakano, M. Tanaka, Y. Nakamira, M. Konno, J.Chem.Eng.Japan 33(5) (2000), 747-752.

[7] N. Tazrouti and M. Amrani, Bioresources, 4(2) (2009), 740-755.

[8] R. Zhang, B. Wang, H. Ma, Desalination, 255 (2010), 61-66.

[9] W.A. Ahmad, Z.A. Zakaria, A.R. Khasim, M.A. Alias, S.M.H.S. Ism ail, Bioresource Technology 101 (2010), 4371-4378.

[10] A.S. Stasinakisa, N.S. Thomaidisa, D. Mamaisb, E.C. Papanikolaoua, A. Tsakona, T.D. Lekkasa, Water Research 37 (2003), 2140-2148.

[11] O.P. Case, (1974).Metallic recovery from wastewaters utilizing cementation, EPA-270/2-74-008, U.S. Washington DC.

[12] U.S.EPA. (1979a). Control Technology for the metal finishing industry-Evaporators, EPA-625/8-79-002, Cincinnati, Ohio.

[13] A.M. Khan, S. Khan, S.A. Ganai, Biology and Medicine 1(2) (2009), 127-133.

[14] E. Bazrafshan, A.H. Mahvi, S. Naseri, A.R. Mesdaghinia, Turkish J. Eng. Env. Sci. 32 (2008), 59-66.

[15] N. Kannan and G. Rengasamy, Water Air Soil Pollut. 163 (2005), 185-201.

[16] B.V. Babu and S. Gupta, Adsorption 14(2007), 85-92.

[17] B.V. Babu, and S. Gupta, J.Environ. Eng. Sci. 7 (2008), 553-557.

[18] V. Vinodhini and N. Das, ARPN Journal of Agricultural and Biological Science 4(6) (2009), 19-23.

[19] A.I. Okoye, P.M. Ejikeme, O.D. Onukwuli, Int. J. Environ. Sci. Tech. 7 (4) (2010), 793-800.

[20] Y.B. Onundi, A.A. Mamun, M.F. Al Khatib, Y.M. Ahmed, Int. J. Environ. Sci. Tech. 7 (4) (2010), 751-758.

[21] C.Y. Yin, M.K. Aroua, W.M.A.W. Daud, Sep. Purif. Technol. 52 (2007), 403-415.

[22] C.K. Ahn, D. Park, S.H. Woo, J.M. Park, Journal of Hazardous Materials 164 (2009), 1130-1136.

[23] A.A. Nunes, A.S. Franca, L.S. Oliveira, Bioresource Technology 100(2009), 1786-1792.

[24] S. Manocha, Sadhana 28 (1 & 2) (2003), 335-348.

[25] W.T. Tsai, C.Y. Chang, S.L. Lee, Bioresource Technology 64 (1998), 211-217.

[26] K. Mohanty, M. Jha, B. C. Meikap, M. N. Biswas, Chemical Engineering Science 60(11) (2005), 3049-3059.

[27] G. J. Alaerts, V. Jitjaturant, P. Kelderman, Water Science and Technology 21(12) (1989), 1701-1704.

[28] M. Kobya, Adsorption Science and Technology 22(1) (2004), 51-64.

[29] H. Hasar, and Y. Cuci, Environmental Technology 21 (2000), 1337-1342.

[30] S. Arivoli, V. Nandhakumar, S. Saravanan, S. Nagarajan, The Arabian Journal for Science and Engineering 34(1A) (2009), 1-12.

[31] E. Demirbas, M. Kobya, E. Senturk, T. Ozkan, Water SA 30 (2004), 533-539.

[32] A.A. Attia, S. A. Khedr, S.A. Elkholy, Brazilian Journal of Chemical Engineering 27(1) (2010), 183-193.

[33] M.H. Isa, N. Ibrahim, H.A. Aziz, M.N. Adlan, N. Sabiani, A.A.L. Zinatizadeh, S.R.M. Kutty, Journal of Hazardous Materials 152 (2008), 662-668.

[34] http://en.wikipedia.org/wiki/Pterospermum_acerifolium

[35] P. Pookmanee, P. Thippraphan, S. Phanichphant, Journal of the Microscopy Society of Thailand 4 (2) (2011), 103-107.

[36] B. Stuart, Modern Infrared Spectro-scopy, (1996). Wiley, Chister, UK.

[37] N. T. Abdel-Ghani, M. Hefny, G. A. F. El-Chaghaby, Int. J. Environ. Sci. Tech. 4 (1) (2007), 67-73.

[38] D. C. Sharma, and C. F. Forster, Water Research, 27(1993), 1201-1208.

[39] K. Selvaraj, V. Chandramohan, S. Pattabhi, Indian Journal of Chemical Technology 18 (1997), 641-646.

[40] H. Cesur and N. Balkaya, Chemical Engineering Journal 131 (2007), 203-208.

[41] S. Nomanbhay and K. Palanisamy, Electronic Journal of Biotechnology 8(1) (2005), 43-53.

[42] D. Park, Y. Yun, H.W. Lee, J.M. Park, Bioresource Technology 99 (2008), 1141-1147.

[43] K. Selvaraj, S. Manonmani, S. Pattabi, Biores. Technol. 89 (2003), 207-211.

[44] D. D. Das, R. Mahapatra, J. Pradhan, S. N. Das, R. S. Thakur, J. Colloid Interface Sci. 232 (2000), 235-240.

[45] D. Donmez and Z. Aksu, Process Biochem. 38 (2002), 751-762.

[46] H. Freundlich, Uber die adsorption in losungen. Zeitschrift fur Physikalische Chemie. 57 (1906), 385-470.

[47] I. Langmuir, Journal of the American Chemical Society 38(1916), 2221-2295.

[48] Z. Hu, L. Lei, Y. Li, Y. Ni, Sep. Purif. Technol. 31(1) (2003), 13-18.

[49]G. Cimino, A. Passerini, G. Toscano, Water Research, 34(11) (2000), 2955-2962. [50]T. Karthikeyan, S. Rajgopal, L.R. Miranda, Journal of Hazardous Materials 124(1-3) (2005), 192-199.

[51] S. Lagergren, kunglia srenska vertens Ka psakademiens Handlingar, Band 24(4) (1898), 1-39.

[52] Y. S. Ho, and G. McKay, Process Biochem. 34 (1999), 451-465.

[53] N. Rajic, D. Stojakovic, M. Jovanovic, N.Z. Logar, M. Mazaj, V. Kaucic, Applied Surface Science 257 (2010), 1521-1532.

[54] M.E. Argun, S. Dursun, M. Karatas, Journal of Hazardous Materials 141, (2007), 77-85.

[55] C. Namasivayam and R.T. Yamuna, Water, Air, and Soil Pollut. 113(1999), 371-384.

[56] S. Qaiser, A. Saleemi, M. Umar, Electronic Journal of Biotechnology 12(4) (2009), 1-17.

[57] G. Karthikeyan and S. Siva ilango, E-Journal of Chemistry 5(4) (2008), 666-678.